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Solar-light-assisted Fenton oxidation of 2,4-dinitrophenol (DNP) using Al_2O_3-supported Fe(III)-5-sulfosalicylic acid (ssal) complex as catalyst

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ABSTRACT

Photoassisted Fenton oxidation of 2,4-dinitrophenol (DNP) was studied in detail using a novel Fe(III)-5-sulfosalicylic acid (ssal) complex loaded Al_2O_3 as catalyst in the presence of H_2O_2 and solar light. The effects of different reaction parameters such as initial pH, catalyst loading, H_2O_2 dosage, initial substrate concentration and temperature on photodegradation were investigated and the optimal operational parameters are reported. The repeatability of photocatalytic activity was also tested. The oxidative degradation of DNP by photo-Fenton-type process in the initiation phase and the fast phase both followed the pseudo-first-order kinetics, and possible reaction mechanisms describing the role of the ligand 5-sulfosalicylic acid and the route of degradation were proposed. The Al_2O_3-supported [Fe(III)-ssal] complex catalyst was found to be very efficient in the decolorization and COD reduction of real wastewater from DNP manufacturing. Thus, this study showed the feasible and potential uses of the catalytic system in oxidative degradation of various organic contaminants and industrial effluents.

1. Introduction

Alkyl dinitrophenols are widely acknowledged to be a group of persistent organic contaminants which show low biodegradability and pose serious risks to human health and the environment. 2,4-Dinitrophenol (DNP) is a typical example of this class of toxic compounds. DNP is mainly used as polymerization inhibitor for vinyl aromatics in petrochemical industry and as a pesticide in agriculture. DNP is released into surface water through its manufacturing and application processes. Although much benefit is obtained from its uses, DNP has some undesirable side effects, such as toxicity and carcinogenity, and its use and the maximum concentration level in water are restricted by the US Environmental Protection Agency (EPA) [1]. Therefore, removal of DNP from aqueous effluents is a significant environmental issue. The more complex environmental problems are that DNP is resistant to biological degradation and can be hardly destroyed in conventional wastewater water treatment technologies, so there is a pressing need to provide a method for the degradation and removal of DNP from the environment which is of low cost and little time consuming.

The advanced oxidation processes (AOPs) have been the efficient available technologies to destroy a wide variety of organic compounds. Among the AOPs, Fenton (Fe^{2+}/H_2O_2) and Fenton-like processes are the most attractive environmental remediation technologies for degradation of persistent organic pollutants in aqueous solution [2]. These processes based on the formation of very active hydroxyl radicals ($^{\bullet}OH$), which react quickly with the pollutants. The generation of $^{\bullet}OH$ radicals and the degradation of the contaminant in the Fenton process are described in Eqs. (1) and (2), respectively [3]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{1}$$

$$k_1 = 51\,M^{-1}\,s^{-1}$$

$$^{\bullet}OH + \text{Pollutants} \rightarrow \text{Degradationproducts} \tag{2}$$

According to reaction (1), Fe^{2+} is oxidized to Fe^{3+} and then regenerated through the reduction of ferric ion by H_2O_2 [4], as shown in Eq. (3):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{3}$$

$$k_3 = 0.001 - 0.01\,M^{-1}\,s^{-1}$$

However, because the reaction rate of Eq. (3) is much slower than that of Eq. (1), the Fe^{2+} ion is quickly consumed, but slowly regenerated [5]. The Fenton reaction slows down due to the low concentration of Fe^{2+} ion, which was reported in the literatures [6]. In order to enhance the regenerated rate of Fe^{2+} ion, chelating agents for iron are introduced into Fenton reactions because the ligands can assist in the catalytic reactions to iron [7,8]. Considering the ability of both heme and non-heme iron enzymes to

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catalyze a wide variety of oxidation transformations under mild conditions in nature, increasing attention has been focused on the use of iron complexes with nitrogen ligands to mimic or emulate the catalytic properties of natural enzymes [9,10]. However, the nitrogenated ligands with a rigid structure often involve in the reactions as electron donors to form porphyrin-resembling ring cation radicals, resulting the direct decomposition and deactivation of the catalysts [11]. The catalytic oxidation of persistent organics promoted by iron complexes with non-nitrogen ligands have been limitedly studied and reported.

Recently, Al_2O_3-supported Fe(III) complex with 5-sulfosalicylic acid (ssal) ligand is found to be an efficient catalyst for the direct hydroxylation of benzene with hydrogen peroxide under visible light irradiation [12]. This novel catalyst of Fe(III) complex with 5-sulfosalicylic acid supported directly on Al_2O_3 can realize the efficient recycling between Fe^{2+}/Fe^{3+} under solar irradiation during the experiments. The present study was undertaken to investigate experimentally the characteristics of the photocatalytic degradation of 2,4-dinitrophenol (DNP) using this catalyst in the presence of H_2O_2 and solar light. The main objective of our work was to investigate the practical applicability of [Fe(III)-ssal]-Al_2O_3 as heterogeneous photo-Fenton-type catalyst for degradation of persistent organic contaminants in water.

2. Experimental

2.1. Materials

The reagent 5-sulfosalicylic acid (ssal) was purchased from Sigma Chemical Co. Ltd. DNP was used as an alkyl dinitrophenol pollutant and obtained from Retell Fine Chemical Co. Ltd. (Tianjin, PRC). All other reagents used in this study, including alumina, nitric acid, sulfuric acid, sodium hydroxide, ascorbic acid, $Fe(NO_3)_3{\cdot}9H_2O$ and H_2O_2 (30% w/w) were of analytical reagent (AR) grade and obtained from Tianjin Kermel Chemical Reagent Co. Ltd., China. Double distilled water was used for preparation of the Al_2O_3-supported [Fe(III)-ssal] complex catalyst. A stock solution containing DNP (1.73×10^{-4} M) was prepared in deionized water. Further DNP aqueous solutions of different concentrations were made using the same stock solution.

A typical procedure for the preparation of Al_2O_3-supported Fe(III)-5-sulfosalicylicacid (ssal) complex catalyst is given below. 5-Sulfosalicylic acid (0.3 mmol) was stirred in a mixture of $Fe(NO_3)_3{\cdot}9H_2O$ (0.6 mmol) and 10 mL of nitric acid (0.5 M) for 1 h at room temperature. The pH value of the mixture was adjusted to about 2.5 using 0.1 M NaOH or 0.1 M H_2SO_4. Afterwards, 1.0 g of Al_2O_3 was slowly added to the mixture and stirred incessantly for 24 h until the color of the mixture disappeared gradually. The mixture was then filtered, and the solid was washed with double distilled water and dried under vacuum. The final product was collected and stored in a vacuum desiccator prior to further use. The w/w loading of Fe onto the [Fe(III)-ssal]-Al_2O_3 catalyst was measured using a UNICAM 969 flame atomic absorption spectrophotometer and the value was found to be 33.18 mg g^{-1}.

2.2. Procedures and analyses

The solar-assisted photocatalytic degradation of DNP was performed on sunny days of May–June 2009 at Experimental Centre of Chemistry, campus building, Dalian University of Technology (38°52′56″N; 121°31′17″E). The experiments were conducted between 11:00 a.m. and 1:00 p.m. when the solar intensity fluctuations were minimal. The variations in the solar light intensity in a day between 11:00 a.m. and 1:00 p.m. were recorded with a radiometer (PC-2, Shanghai JWFU Industry Co. Ltd., China) and the average light intensity over the duration of each experiment was calculated to be 0.532 kW m^{-2}. The reaction temperature was controlled by a super constant temperature water trough (CHS-10A, Suzhou Instrument Manufacturing Co. Ltd., China). The conical borosilicate flask capped with glass stopper of 250 mL capacity, 140 mm height, 0.8 mm thick, 32 mm neck diameter and 82 mm bottom diameter was used as photoreactor in the solar experiments. Considering the fact that the wall of the photoreactor is very thin, the amount of solar light absorbed by the photoreactor can be negligible.

In all cases, 100 mL of the DNP solution containing appropriate quantity of the [Fe(III)-ssal]-Al_2O_3 and H_2O_2 suspensions were used. After stirring continuously in the dark for 2 min, the suspension was irradiated by sunlight and it was treated as the starting point ($t = 0$) of the reaction, where the concentration of DNP was designated as C_0. During the experimental run, 10 mL of the reacting solution was withdrawn from the reactor at specific time intervals. For analysis, ascorbic acid was added to the sample immediately to stop any further oxidation reaction. The samples were then centrifuged immediately at $1620 \times g$ for 10 min to remove the catalysts particles and subjected to analysis. The concentration of DNP (C) solution during the oxidation process was monitored through measuring the absorbance of the solution samples with UV–vis spectrophotometer at $\lambda_{max} = 357$ nm using a calibration curve [13]. The DNP removal was calculated using the equation given below:

$$\text{Removal (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (4)$$

where C_0 and C are the concentration of DNP at $t = 0$ and t, respectively.

UV–vis spectral analysis was done using Rayleigh UV1201 UV–vis spectrophotometer (Beijing Rayleigh Analytical Instrument Corp., China) in the range of 190–850 nm. The pH of the solution is measured using a Mettler-Toledo (model Delta 320-S) digital pH meter.

3. Results and discussion

3.1. Primary experiments

The DNP (30 mg L^{-1}) was taken with 1.0 g L^{-1} [Fe(III)-ssal]-Al_2O_3 catalyst and stirred for 2 h in dark. The DNP adsorption on the catalyst was measured firstly after the establishment of adsorption/desorption equilibrium of DNP. It was observed that there was no significant change in concentration of the DNP. The experimental result shows that there is almost no adsorption of DNP and DNP adsorption on [Fe(III)-ssal]-Al_2O_3 catalyst can be negligible during the photo-Fenton process.

The solar photocatalytic activity of Al_2O_3-supported [Fe(III)-ssal] catalyst was evaluated by the degradation of DNP under different reaction conditions and the results are displayed in Fig. 1. The DNP when irradiated with [Fe(III)-ssal]-Al_2O_3 in the absence of H_2O_2 does not undergo degradation up to 70 min (curve e). It means DNP is resistant to self-photolysis by solar light. A very small decrease in DNP concentration occurred when it was treated with H_2O_2/solar light (curve d) and [Fe(III)-ssal]-Al_2O_3/H_2O_2/dark (curve c).

In order to compare [Fe(III)-ssal]-Al_2O_3/H_2O_2 photo-Fenton degradation with that of typical Fe(III)-Al_2O_3/H_2O_2 photo-Fenton process, the degradation was conducted by taking the same amount of Fe^{3+} (from ferric nitrate nonahydrate) and Al_2O_3 used in the preparation of [Fe(III)-ssal]-Al_2O_3 photo-Fenton catalyst. The DNP on irradiation with solar light using [Fe(III)-ssal]-Al_2O_3/H_2O_2 undergoes fast and complete degradation in 70 min (curve a) when compared with Fe(III)-Al_2O_3/H_2O_2 system (curve b). The characteristic absorbance band of DNP at 357 nm in the visible region

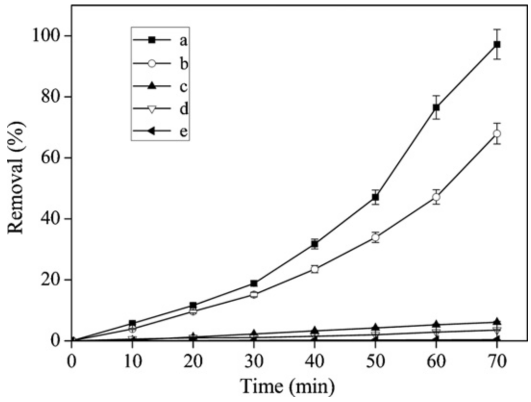

Fig. 1. Degradation of DNP under various conditions: (a) DNP/[Fe(III)-ssal]-Al_2O_3/H_2O_2/solar; (b)DNP/Fe(III)-Al_2O_3/H_2O_2/solar; (c) DNP/[Fe(III)-ssal]-Al_2O_3/H_2O_2/dark; (d) DNP/H_2O_2/solar; (e) DNP/[Fe(III)-ssal]-Al_2O_3/solar.

progressively disappeared upon irradiation up to 70 min when it was treated with [Fe(III)-ssal]-Al_2O_3/H_2O_2 (Fig. 2). The result indicates that the photocatalytic activity of [Fe(III)-ssal]-Al_2O_3 is better than that of Fe(III)-Al_2O_3 for DNP degradation in the presence of solar light and H_2O_2.

3.2. *Effect of pH*

pH is an important parameter in heterophoto-Fenton reactions. Therefore, the effect of pH on the degradation of DNP was investigated by keeping all other experimental conditions constant and varying the initial pH of the DNP solution from 2.5 to 7.3. The experiments were carried out using DNP solutions with various pH values determined initially and without any modifications or control of the pH during the process. The results are depicted in Fig. 3. The removal of DNP decreased with increase in pH value from 2.5 to 7.3. The maximum degradation of DNP was observed within 70 min at pH 2.5. Hence pH 2.5 is optimum for the heterogeneous photo-Fenton degradation of DNP. Above pH 2.5, the efficiency of the photo-Fenton process decreases due to the coagulation of hydroxo complex of Fe ions formed during the reaction.

The maximum DNP removal was observed at acidic pH similar to traditional homogeneous Fenton process, which indicates that the mechanism of degradation is same for both heterogeneous and homogeneous degradations. During experiments, pH dropped from the initial values to about 4 in case of pH > 3, whereas the pH value remained almost unchanged during the process at initial pH 2.5. This can be attributed to the destruction of DNP into organic acids as the degradation proceeds, leading to a drop of pH of the solution and consequently to an acceleration of the removal process.

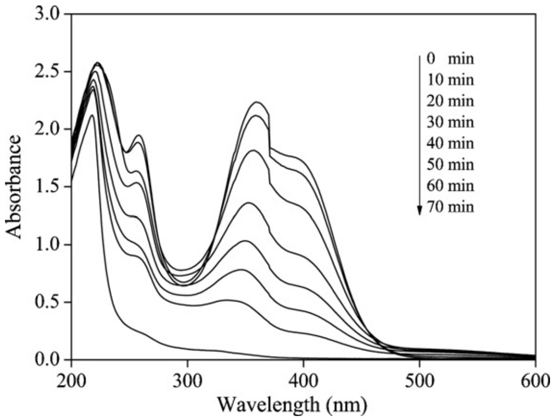

Fig. 2. Time dependent UV–vis absorbance spectra of DNP.

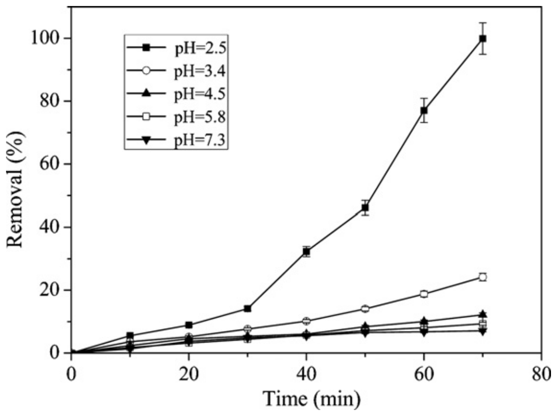

Fig. 3. Effect of solution pH: [DNP] = 30 mg L^{-1}, catalyst loading = 1.0 g L^{-1}, H_2O_2 dosage = 2.5 mmol L^{-1}, 30 °C.

3.3. *Effect of H_2O_2 dosage*

The removal of DNP with Al_2O_3-supported [Fe(III)-ssal] at pH 2.5 at different H_2O_2 concentrations was studied. The results are presented in Fig. 4. Up to 2.5 mmol L^{-1} concentration of H_2O_2, the degradation was significantly increased and after that a decline in degradation was observed, indicating an optimum H_2O_2 dosage of approximately 2.5 mmol L^{-1} for best performance. The enhancement of degradation by the addition of H_2O_2 is due to the increased production of $^{\bullet}OH$ radicals [14]:

$$H_2O_2 + e_{CB}^{-} \rightarrow {}^{\bullet}OH + OH^{-} \quad (5)$$

$$H_2O_2 + O_2 \rightarrow {}^{\bullet}OH + H^{+} + O_2 \quad (6)$$

Addition of H_2O_2 above 2.5 mmol L^{-1} did not improve the degradation. This could be because the generated hydroxyl radicals produced hydroperoxyl radicals ($HO_2^{\bullet}$) in the presence of a local excess of H_2O_2 as shown in Eqs. (7) and (8), consequently lowering the hydroxyl radical concentration [15,16]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (7)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (8)$$

The $HO_2^{\bullet}$ radicals are much less reactive and do not contribute to the oxidative degradation of the organic substrate which occurs only by reaction with $^{\bullet}OH$. Therefore it can be concluded that a H_2O_2 dosage higher than 2.5 mmol L^{-1} corresponds to unnecessary

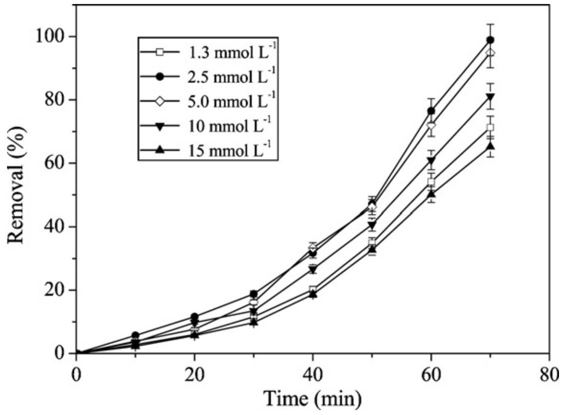

Fig. 4. Effect of H_2O_2 dosage: [DNP] = 30 mg L^{-1}, catalyst loading = 1.0 g L^{-1}, pH = 2.5 ± 0.1, 30 °C.

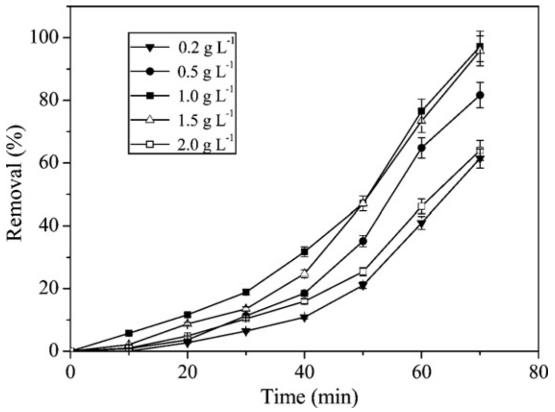

Fig. 5. Effect of catalyst loading: [DNP] = 30 mg L^{-1}, H_2O_2 dosage = 2.5 mmol L^{-1}, pH = 2.5 ± 0.1, 30 °C.

consumption of hydrogen peroxide. The addition of H_2O_2 up to 2.5 mmol L^{-1} showed a beneficial effect on the removal of DNP.

3.4. *Effect of catalyst loading*

The effect of catalyst loading on the removal of DNP was investigated by keeping all other experimental parameters constant (Fig. 5). The removal of DNP increased with increase in catalyst concentration from 0.2 to 1.0 g L^{-1}. Increase of the catalyst concentration more than 1.0 g L^{-1} resulted in the decrease of degradation efficiency. This could be due to $^{\bullet}$OH radicals are scavenged by reaction with higher concentration of Fe(II) [5]:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (9)$$

Further, the higher catalyst concentration prevents the efficient light absorption in the solution. Therefore an optimum concentration of the catalyst can enhance the degradation and the catalyst loading of 1.0 g L^{-1} was selected for further experiment.

3.5. *Effect of initial DNP concentration*

The effect of initial concentration of DNP on the removal process was investigated over the concentration range from 17 mg L^{-1} to 30 mg L^{-1} with constant weight of the catalyst (1.0 g L^{-1}) and H_2O_2 dosage (2.5 mmol L^{-1}). The removal of DNP decreased as the initial concentration of DNP increased under 70 min of solar irradiation (Fig. 6). The removal of DNP is directly proportional to the probability of $^{\bullet}$OH radicals reacting with the DNP molecules. Since the concentration of the catalyst, amount of H_2O_2 and the solar light power are same for all DNP concentration, the generation of $^{\bullet}$OH radicals remains constant. As the initial concentration of DNP increases, the interaction of $^{\bullet}$OH radical with DNP decreases. Further, the increase in DNP concentration also decreases the path length of photon entering into the solution and the relative formation of $^{\bullet}$OH radicals decreases leading to the decreased photo-Fenton degradation efficiency.

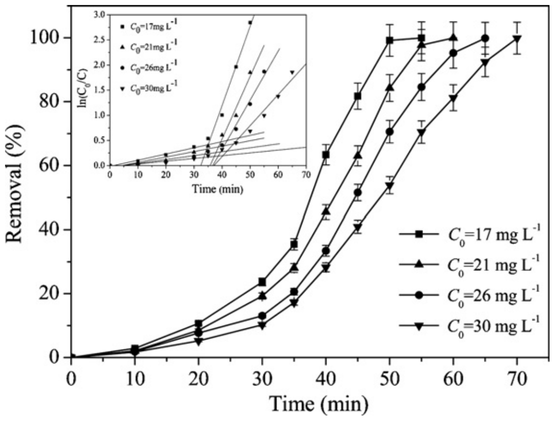

Fig. 6. Effect of initial DNP concentration: H_2O_2 dosage = 2.5 mmol L^{-1}, catalyst loading = 1.0 g L^{-1}, pH = 2.5 ± 0.1, 30 °C. The figure inset shows DNP degradation kinetics ($\ln(C_0/C)$ versus treatment time plot for 70 min) obtained for the same experiments.

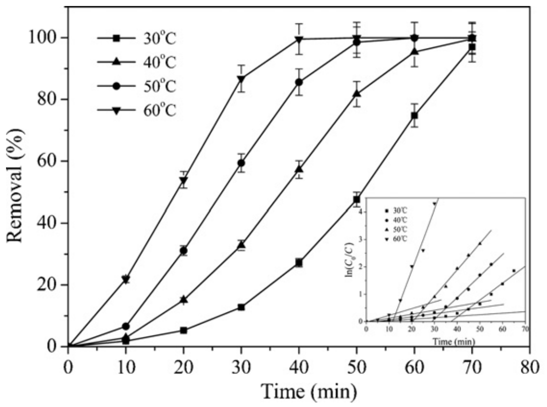

Fig. 7. Effect of reaction temperature on DNP removal: [DNP] = 30 mg L^{-1}, H_2O_2 dosage = 2.5 mmol L^{-1}, catalyst loading = 1.0 g L^{-1}, pH = 2.5 ± 0.1. The figure inset shows DNP degradation kinetics ($\ln(C_0/C)$ versus treatment time plot for 70 min) at different temperatures obtained for the same experiments.

The degradation of DNP by [Fe(III)-ssal]-Al_2O_3/H_2O_2 photo-Fenton reaction was a two-phase reaction: the initiation phase and the fast phase. At the first 35 min the degradation of 30 mg L^{-1} DNP was slow and only 17% DNP removal was achieved. However, the degradation rate increased quickly after 35 min and the removal of DNP reached 99.72% at 70 min. The degradation of DNP in the initiation phase and the fast phase fitted the following pseudo-first-order kinetics:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (10)$$

where C_0 and C is the concentration of DNP at the initial time and at the reaction time t, respectively; k is the pseudo-first-order reaction rate constant (min^{-1}). The Fig. 6 inset shows $\ln(C_0/C)$ versus reaction time t plot for 70 min obtained for the same experiments. It was found that at the beginning of the reaction, the plot of the first several data point of $\ln(C_0/C)$ (A) versus time fitted linear. And the next several data points (B) versus time fitted another straight line. The interval including data (A) can be defined as the initiation period [17]. The two linear plots will yield slopes of the observed rate constants in the initiation phase (k_A) and the fast phase (k_B), respectively. The calculation results showed that increase of the initial DNP concentration from 17 to 30 mg L^{-1} decreases the pseudo-first-order rate constant from 1.23×10^{-2} to 5.51×10^{-3} min^{-1} in the initiation phase and from 1.57×10^{-2} to 6.16×10^{-2} min^{-1} in the fast phase.

3.6. *Effect of the reaction temperature*

The effect of temperature was investigated under the optimized experimental conditions by varying the temperature range from 30 to 60 °C (Fig. 7). The DNP removal increased steadily at enhanced temperature up to 60 °C. The results indicate that increased temperature can accelerate the photocatalytic performance of the Al_2O_3-supported [Fe(III)-ssal] complex catalyst. The increase in DNP removal with increasing temperature might be due to the accelerated decomposition of H_2O_2 into $^{\bullet}$OH radicals and the increased number of active surface centers available for reaction at higher temperatures. The degradation of DNP at different temperatures can also be divided into the initiation phase and the fast phase.

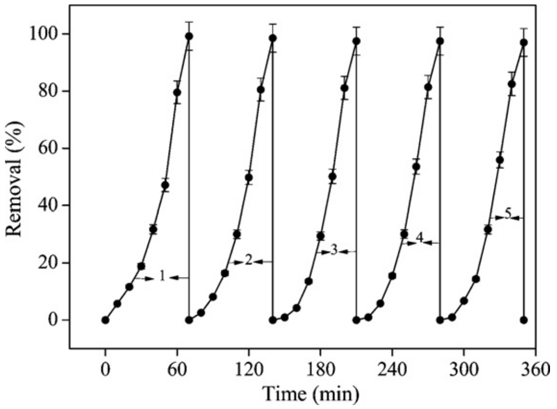

Fig. 8. Repetitive use of the [Fe(III)-ssal]-Al_2O_3 photo-Fenton catalyst.

The degradation of DNP in the initiation phase and the fast phase at different temperatures both followed a first order law (Fig. 7 inset). Data of these observed kinetics for the degradation of DNP at different temperatures indicates that increase of the temperature from 30 to 60 °C, the observed rate constants k_A from 5.51×10^{-3} to 2.47×10^{-2} min^{-1} and k_B from 6.16×10^{-2} to 2.23×10^{-1} min^{-1}, which means that the increase of reaction temperature can shorten the initiation period and increase the corresponding observed rate constants in the initiation phase and the fast phase.

3.7. Recycling studies

The catalyst's lifetime is an important parameter of the photo-Fenton process, due to the fact that its use for longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled five times using DNP solutions at optimum conditions. After each experiment, the catalyst was separated from solution by filtration, washed with deionized water for several times, dried at 40 °C for over night and then used for next run. Noticeably, after five cycles of experimentation, the catalysis efficiency of the [Fe(III)-ssal]-Al_2O_3 catalyst was still higher than 97%, and the catalytic performance was not affected by the times of reuse (Fig. 8). The decay of active catalytic sites is considered as the main reason for the loss of catalytic activity because of small amounts of leached iron from catalyst surface [18]. The stable performance of the [Fe(III)-ssal]-Al_2O_3 catalyst revealed that the leached iron from the catalyst during each run can be negligible.

3.8. Postulated reaction mechanism

Based on the above investigation, the following mechanism is proposed for [Fe(III)-ssal]-Al_2O_3-supported photo-Fenton degradation (Fig. 9).

The ligand 5-sulfosalicylic acid in Fe(II)-ssal-Al_2O_3 catalyst can be regarded as a hydroquinone-like compound. Upon visible light irradiation, 5-sulfosalicylic acid (compound I) can be excited to form a transition state, which will reduce Fe^{3+} to Fe^{2+} by metal-ligand charge transfer process (see II and III in Fig. 9) [19]. The free Fe^{2+} ions will be released into the solution because of the weak forces between Fe^{2+} and 5-sulfosalicylic acid, which triggers the corresponding Fenton reaction. The generated •OH radicals in the photo-Fenton process attack DNP pollutant giving rise to degradation products. In the initiation phase, the generation of Fe^{2+} was too small to cause the fast degradation of DNP. The ligand still immobilized alumina (compound IV) will not be attacked by •OH radicals, which can combine with the Fe^{3+} ions produced in the initiation period and reduce Fe^{3+} to Fe^{2+} again, resulting in the regeneration of Fe^{2+} in the solution. The role of 5-sulfosalicylic acid keeps Fe^{2+} ion being regenerated and accelerates the Fe^{3+}/Fe^{2+} circle. Compared with the initiation phase, the consumption of H_2O_2 and the generation of Fe^{2+} increased in the fast phase. The quick formation of Fe^{2+} in the fast phase was not due to the reaction of Fe^{3+}/Fe^{2} with the inorganic species including H_2O_2, •OH, HO_2• and O_2^{-}• but the reduction of Fe^{3+} by the ligand 5-sulfosalicylic acid [20].

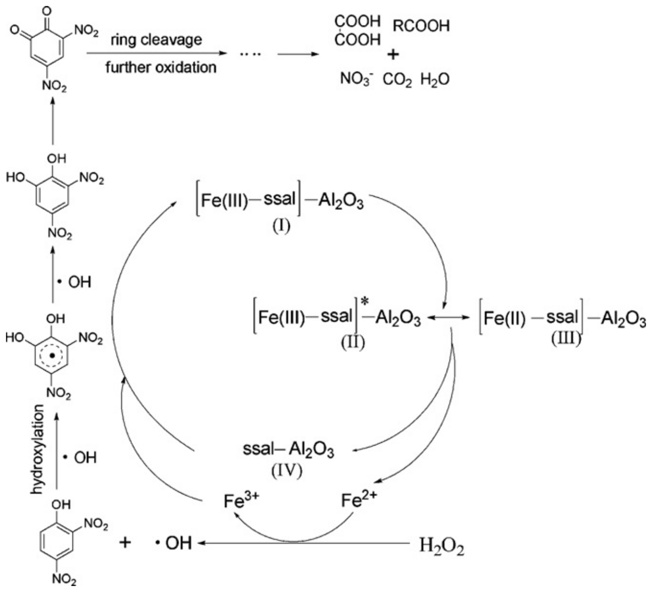

Fig. 9. A pictorial representation of photo-Fenton degradation of DNP over [Fe(III)-ssal]-Al_2O_3 catalyst.

In order for full understanding of the role played by the ligand 5-sulfosalicylic acid, the amount of •OH radicals formed by [Fe(III)-ssal]-Al_2O_3/H_2O_2 and Fe(III)-Al_2O_3/H_2O_2 photo-Fenton system was determined respectively. The generated •OH radicals were determined according to the spectrophotometric method using methyl violet as a colored indicator of hydroxyl radical production described in Zhang et al. [21]. Quantitative determinations of its hydroxylated products can be performed using colorimetry. The change in absorbance, ΔA, corresponding to color intensity change of methyl violet was measured at $\lambda = 584$ nm and used to indicate the amount of •OH produced indirectly. Experimental studies of methyl violet decoloration with [Fe(III)-ssal]-Al_2O_3 and Fe(III)-Al_2O_3 catalysts were conducted using the following conditions: 2.45×10^{-2} mmol L^{-1} methyl violet concentration, pH 2.5, 30 °C, 2.5 mmol L^{-1} H_2O_2 and the same amount of Fe^{3+} (0.125 mmol L^{-1}). Compared with Fe(III)-Al_2O_3/H_2O_2 system, the amount of •OH radicals increased greatly for [Fe(III)-ssal]-Al_2O_3/H_2O_2 system by introducing the ligand 5-sulfosalicylic acid, hence color intensity change of methyl violet was efficiently enhanced (Fig. 10). This indicates the importance of 5-sulfosalicylic acid in the corresponding heterogeneous photo-Fenton catalytic reactions. The ligand 5-sulfosalicylic acid can enhance the catalytic efficiency and promote the circulation of photo-Fenton catalyst.

In the Fenton process, oxidative degradation of DNP occurs generally by the attack of •OH radicals, known as highly reactive electrophilic oxidants. The attack of electrophilic •OH radical occurs at ring position activated by the presence of three substituents in DNP. Based on these, though intermediates forming in the photocatalytic degradation process of DNP are not identified, the mechanism suggested by Kavitha and Palanivelu [22] and Lu and coworkers [23] is also postulated in our system. The electron-donating substituent, phenolic hydroxyl group, increases the electron density at *ortho* and *para* positions, so the electrophilic attack will occur preferentially in *ortho* and *para* positions with respect to phenolic hydroxyl group, resulting in hydroxylated

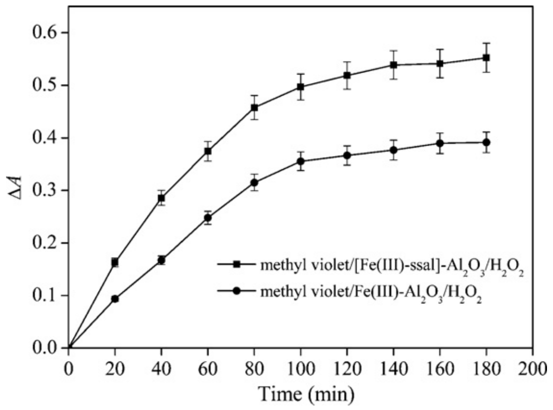

Fig. 10. The influence of various photo-Fenton catalysts on •OH productivity.

dinitrophenols through the formation of dihydroxynitrocyclohexadienyl radicals. On subsequent •OH radical attack, these primary hydroxylated dinitrophenols forms species with higher oxygen to carbon content. In turn, they may be subjected to further attack by •OH radical, eventually leading to aromatic ring opening and the formation of a series of small molecules like acetic and oxalic acids et al. Finally, the reaction intermediates are mineralized into CO_2, H_2O and $NO_3{}^-$.

3.9. Photocatalytic oxidation of wastewater from DNP manufacturing

From a practical point of view, there is a need to investigate the application of the [Fe(III)-ssal]-Al_2O_3/H_2O_2 system for the degradation of nitrophenols from real wastewater under solar irradiation. We conducted a study to determine the potential use of the [Fe(III)-ssal]-Al_2O_3 catalyst for decolorization and chemical oxygen demand (COD) reduction of wastewater from DNP manufacturing. The original wastewater with orange red color for the experiments was provided by Tairui, Inc. (Dalian, China). The COD and the color of the samples are estimated by dichromate method and the Platinum-Cobalt Standard method, respectively [24]. Results from analyses of the wastewater are given in the recent published literature [13]. Experiments were carried out using the real wastewater with 0.15% w/v [Fe(III)-ssal]-Al_2O_3 catalyst, 0.02% w/v H_2O_2 and 120 min solar irradiation to investigate the removal of color and reduction in COD. The removal of COD and decrease in color for the wastewater in 120 min of solar irradiation were 82% and 86%, respectively, which confirms the destruction of the organic molecules in the wastewater. Since industrial wastewaters such as the one examined in this study contain a complex combination of chemicals compounds, the photo-Fenton catalyst [Fe(III)-ssal]-Al_2O_3 is hopeful to be used in degradation of various toxic organic contaminants.

4. Conclusions

In conclusion, this study has proved that Fe(III) complex with hydroquinone-like ligand 5-sulfosalicylic acid [Fe(III)-ssal] immobilized alumina is an efficient photo-Fenton catalyst for degradation of 2,4-dinitrophenol (DNP) in the presence of H_2O_2 and solar light. The optimal reaction conditions for the photocatalytic degradation of DNP were determined to be: 30 °C, pH 2.5, 1.0 g L^{-1} [Fe(III)-ssal]-Al_2O catalyst loading, 2.5 mmol L^{-1} H_2O_2 dosage and 70 min solar irradiation time. The degradation of DNP in the photo-Fenton process can be divided the initiation phase and the fast phase, which both followed the pseudo-first-order kinetics with respect to the concentration of DNP. The pseudo-first-order reaction rate constant increased with an increase in temperature. No obvious decline in efficiency of the catalyst was observed after five repeated cycles and this demonstrated the stability and reusability of the catalyst. The catalyst prepared was found to be very effective in the decolorization and COD reduction of real wastewater from DNP manufacturing and this made the application of [Fe(III)-ssal]-Al_2O catalyst for degrading various organic pollutants and industrial effluents under solar irradiation more practical.

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